

INSECTICIDE
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A DIGEST OF INFORMATION ON HEXAETHYL TETRAPHOSPHATE

R. C. Roark
Division of Insecticide Investigations

The insecticidal properties of hexaethyl tetraphosphate were discovered in Germany and were brought to the attention of the American public by Hall (6) and Kilgore (8, 9) following their visits to Germany in the summer of 1945. In 1946 the production of this compound in the United States was started (1), and entomologists tested it against many kinds of insects in California, Oregon, Wisconsin, New York, and Maryland. It has been reported to be effective against aphids, mites, leafhoppers, thrips, and many caterpillars. It is highly toxic to warm-blooded animals and is rapidly absorbed through the skin. It and the formulations should be handled with caution. It decomposes and loses toxicity on standing in the presence of moisture. The compound, now manufactured on a commercial scale, is currently quoted at \$2.00 per pound in carboys and \$1.10 per pound in drums.

The purpose of this digest is to summarize our present information concerning this compound, for the guidance of entomologists, insecticide manufacturers, and others interested in pest control.

PREPARATION OF HEXAETHYL TETRAPHOSPHATE

In an application for a German patent filed August 4, 1938, Schrader (10) described the preparation of this compound as follows: 182 grams of triethylphosphate are heated while stirring under reflux so that the temperature of the liquid is about 150°C. Within half an hour 53 grams (1/3 mole) of phosphorus oxychloride is added drop by drop. After another half hour at this temperature the mixture is cooled, and 164 grams of the tetraphosphoric acid hexaethyl ester is thus obtained. Yield: 96 percent.

The reaction is $\text{POCl}_3 + 3(\text{C}_2\text{H}_5)_3\text{PO}_4 = (\text{C}_2\text{H}_5)_6\text{P}_4\text{O}_{13} + 3\text{C}_2\text{H}_5\text{Cl}$.

A different process is described by Woodstock (15) in a United States patent application filed August 6, 1942: 156 grams of phosphorus pentoxide are slowly added to 400 grams of triethyl orthophosphate in a water-jacketed reaction vessel equipped with an agitator. Initial cooling of the mixture may be necessary if the phosphorus pentoxide is added too rapidly. The product is a viscous liquid, sp. gr. 1.28, index of refraction 1.425, and it has a decomposition point of approximately 145-150°C.

The reaction is $2(\text{C}_2\text{H}_5)_3\text{PO}_4 + \text{P}_2\text{O}_5 = (\text{C}_2\text{H}_5)_6\text{P}_4\text{O}_{13}$.

PHYSICAL AND CHEMICAL PROPERTIES

Hexaethyl tetraphosphate has the empirical formula $\text{C}_{12}\text{H}_{30}\text{O}_{13}\text{P}_4$, and a structural formula for it has been proposed by Schrader (10, 11). Its molecular weight is 506.28.

Hexaethyl tetraphosphate prepared in glass according to the Schrader process was a light amber-colored oily liquid, sp. gr. (27°/4°C.) 1.2917; refractive index (n_D^{27}) 1.4273. The yield was 99 percent of theory. On distillation of some of the product in vacuo, it decomposed with evolution of ethylene. In the absence of moisture the product is stable at ordinary temperatures, no change in density or refractive index being observed after 6 months.--Bronson and Hall (4).

The commercially prepared unrefined ester is an amber-colored liquid, having a specific gravity of 1.28 or weighing 10.66 pounds per U.S. gallon. It solidifies at about -40°C. and decomposes at temperatures above 150°. It is miscible in water, acetone, alcohol, carbon tetrachloride, chloroform, diacetone alcohol, ethyl acetate, glycerol, o-dichlorobenzene, pine oil, benzene, toluene, xylene, and alkyl naphthalenes, but it is not miscible in kerosene or petroleum ether.--Bronson and Hall (4).

MANUFACTURE

Hexaethyl tetraphosphate was made by the I. G. Farbenindustrie at Leverkusen, Germany, by mixing 1 mole of phosphorus oxychloride with slightly more than 3 moles of triethyl phosphate and blowing the mixture to the top of a column packed with Raschig rings with a reaction kettle at the bottom, the system being kept at 140°C. The product flowed to a cooler of lead coil. The time of the reaction was 1/2 hour and the yield almost quantitative.--Hall (6); Smadel and Curtis (13); Hordtt (7).

The reaction time was 1.5 hours at 140-145°C. Since the reaction product could not be distilled without decomposition, it was continuously drawn off the bottom of the kettle as a crude residue.--Kilgore (9).

FORMULATIONS

In Germany 70 parts of the crude ester was mixed with 30 parts of the emulsifying agent Ho 2406 (polyhydroxyethylated isooctylphenol type) to form an emulsifiable concentrate called Bladan.--Kilgore (8).

Bladan consists of 60 percent of the crude ester, 20 percent of toluene (or xylene or other solvent), and 20 percent of wetting agent.

Nekal (sodium alkyl naphthalenesulfonate) is not satisfactory.--Hall (6); Smadel and Curtis (13).

Bladan is stated to be the hexamethyl (not ethyl) ester of tetraphosphoric acid.--Curtis and Fogler (5).

STABILITY

Undiluted hexaethyl tetraphosphate is stable at room temperature, but is hydrolyzed readily when in contact with water, and the hydrolysis products have little or no insecticidal value. For this reason the warning is given to use it immediately after dilution.--Kilgore (9).

The ester is almost completely hydrolyzed on standing in water for 24 hours, and the solution should be made up just before it is to be used as a spray.--Hall (6).

EFFECT ON METALS

Hexaethyl tetraphosphate in the absence of water did not appreciably corrode strips of brass or iron. However, in the presence of a small proportion of water a very strong acid was formed at once, which rapidly attacked galvanized iron; it also attacked iron but at a much slower rate; it did not attack brass appreciably. A water solution containing 0.1 percent of hexaethyl tetraphosphate (pH 2.45) did not appreciably corrode strips of brass or iron after 106 hours at 25-30°C. After 4 hours at 30°C. approximately 60 percent of the galvanizing was removed from galvanized iron.--Bronson and Hall (4).

EFFECT ON PLANTS

Hexaethyl tetraphosphate aerosols have been applied to 133 plant species, but injury has been detected in only 2, the chrysanthemum and the tomato. In experiments on more than 100 varieties of chrysanthemums injury was apparent in 28 varieties when treated at low temperatures. At high temperatures a trace of injury was detected in only 1, the variety Nevada. Among 3 varieties of tomato, Marglobe and U. S. 24 showed variable degrees of leaf injury and Washington State Forcing only a trace. Since Marglobe tomatoes have been treated repeatedly with hexaethyl tetraphosphate at temperatures held between 72 and 74°F. with no injury, and since the most tender chrysanthemum variety (Nevada) treated at 70°F. developed only a trace of spotting, it appears that even these crops can be treated with this chemical in aerosols.--Smith et al. (14).

TOXICITY TO MAMMALS

The ester is very toxic (to man) and must be handled in bulk with care.--Kilgore (8).

PATENTS

The hexaesters of tetraphosphoric acid, hitherto unknown, are claimed. Claim is also made for the process of making them, comprising heating a phosphorus oxyhalogenide (e. g., phosphorus oxychloride) with a neutral phosphoric acid alkyl ester (e. g., triethyl phosphate) in a molar ratio of about 1:3 under refluxing conditions at atmospheric pressure. The products are water-soluble oils which cannot be distilled without decomposition. They have a glycerol-like consistency and may be used as lubricants or softeners. Esters mentioned are ethyl, n-butyl, 2-chloroethyl, n-dodecyl, n-propyl, 2-methoxyethyl, and cyclohexyl.--Schrader (10, 11).

A method of producing a neutral ester of a molecularly dehydrated phosphoric acid comprises reacting an anhydrous tri-ester of ortho-phosphoric acid with a selected reacting proportion of phosphorus pentoxide from 1/4 to 1 times the molecular equivalent of trialkyl ortho-phosphate ester. The reaction may be carried out in an inert liquid medium, such as toluene, chloroform, or carbon tetrachloride. The preparation and properties of the ethyl and octyl tetraphosphates are described. The specific gravity of hexaethyl tetraphosphate is stated to be 1.280 and its refractive index 1.425.--Woodstock (16).

INSECTICIDAL VALUE

Laboratory tests made at Beltsville have shown no significant difference in toxicity to insects between hexaethyl tetraphosphate made by the Schrader process and that made by the Woodstock process, or between commercially prepared material and that prepared in the laboratory. The influence of the type of formulation of hexaethyl tetraphosphate on its insecticidal effectiveness has not been gone into by experimenters and should be carefully tested. Commercial formulations now on the market are made up with 50 percent of the ester. All concentrations of insecticide mentioned in this digest have been converted to those of the hexaethyl tetraphosphate and not of the formulation, and all aqueous solutions were tested immediately after their preparation.

THEYSANOPTERA

Thripidae

Heliothrips haemorrhoidalis (Bouche), the greenhouse thrips

In laboratory tests by Metcalf in California, the median lethal concentration of hexaethyl tetraphosphate against this thrips was 0.01 percent.--Bishopp (3).

HOMOPTERA

Aleyrodidae

Trialeurodes vaporariorum (Westw.), the greenhouse whitefly

In greenhouse tests 0.3 gram of hexaethyl tetraphosphate per 1,000 cubic feet distributed as an aerosol from a 10-percent solution in methyl chloride killed 100 percent of the white flies.--Smith et al. (14).

Aphidae

Anuraphis halichrysi (Kalt.)

In greenhouse tests 1 to 2.5 grams of hexaethyl tetraphosphate per 1,000 cubic feet, distributed as an aerosol from a 10-percent solution in methyl chloride, killed 99 percent of these aphids.--Smith et al. (14).

Aphis gossypii Glov., the melon aphid

In laboratory tests an aqueous solution of 0.025 percent of hexaethyl tetraphosphate and 0.05 percent of sodium lauryl sulfate caused 100 percent mortality.--Siegler and Hall (12).

In greenhouse tests 0.3 gram of hexaethyl tetraphosphate per 1,000 cubic feet distributed as an aerosol from a 10-percent solution in methyl chloride killed 99 percent of the aphids, and twice this concentration killed 100 percent.--Smith et al. (14).

Aphis pomi Deg., the apple aphid

In laboratory tests an aqueous solution containing 0.10 percent of hexaethyl tetraphosphate and 0.05 percent of sodium lauryl sulfate caused 96 percent mortality.--Siegler and Hall (12).

Aphis fabae Scop., the bean aphid

Field tests in Oregon against the bean aphid on stringless pole beans with a dust containing 3 percent of hexaethyl tetraphosphate at the rate of 40 pounds per acre gave 62 percent control. A 4-percent nicotine sulfate dust gave the same control. The weather was cloudy and the temperature 64°F.--Hanna (*)

1/ An asterisk (*) indicates that a paper was read at the meeting of the American Association of Economic Entomologists at Richmond, Va., December 9-12, 1946, but has not yet been published.

Brevicoryne brassicae (L.), the cabbage aphid

In laboratory tests an aqueous solution of 0.10 percent of hexaethyl tetraphosphate plus 0.05 percent of sodium lauryl sulfate caused 100-percent mortality.--Siegler and Hall (12).

Field tests in Oregon on cauliflower with a dust containing 3 percent of hexaethyl tetraphosphate at the rate of 45 pounds per acre gave 64 percent control. A dust containing 4 percent of nicotine sulfate and 20 percent of calcium arsenate gave 83 percent control. The temperature was 68°F. A dust containing 3 percent of hexaethyl tetraphosphate, 20 percent of sulfur, and 2 percent of DDT gave 68 and 90 percent control in different tests; increasing the hexaethyl tetraphosphate content of this mixture to 5 percent resulted in no better control.--Hanna (*).

In field trials made in Wisconsin, hexaethyl tetraphosphate both as sprays (1 pint in 100 gallons of water) and as freshly prepared dusts (5 percent in pyrophyllite), gave excellent control of the cabbage aphid under both cool and warm conditions. They killed aphids quickly and showed some fumigant action by affecting insects enclosed in rolled leaves. Both dusts and sprays deteriorated rapidly on aging. Little or no toxicity was left by the fourth day. Hexaethyl tetraphosphate in sprays was equally effective with or without an emulsifier. In a hexaethyl tetraphosphate-DDT combination neither material affected the insecticidal value of the other.--Allen and Chapman (*).

In greenhouse tests hexaethyl tetraphosphate emulsified in water with polyethylene glycol monoisooctylphenyl ether at a concentration of 0.6 percent killed 88 percent of the cabbage aphids on potted cabbage plants in 24 hours, whereas nicotine sulfate at 0.8 percent of nicotine killed only 13 percent. A talc dust containing 3 percent of the ester was also effective when freshly prepared but lost its toxicity on standing.--Bronson and Hall (4).

Macrosiphoniella sanborni (Gill.), the chrysanthemum aphid

In laboratory tests an aqueous solution of 0.10 percent of hexaethyl tetraphosphate and 0.05 percent of sodium lauryl sulfate caused 100-percent mortality.--Siegler and Hall (12).

In greenhouse tests 0.3 gram of hexaethyl tetraphosphate per 1,000 cubic feet distributed as an aerosol from a 10-percent solution in methyl chloride killed 97 percent of the aphids, and twice this concentration killed 100 percent.--Smith et al. (14).

Macrosiphum ambrosiae (Thos.), the helianthus aphid

In laboratory tests an aqueous solution of 0.05 percent of hexaethyl tetraphosphate and 0.05 percent of sodium lauryl sulfate caused 100-percent mortality.--Siegler and Hall (12).

Macrosiphum pisi (Kltb.), the pea aphid

In greenhouse tests an emulsion containing 2.4 percent of the ester killed 94 percent of the aphids in 24 hours, whereas 2 percent of nicotine as the alkaloid killed only 3 to 4 percent. Freshly prepared dusts containing 3 percent of the ester killed 90 to 99 percent of the pea aphids.--Bronson and Hall (4).

Macrosiphum solanifolii (Ashm.), the potato aphid

Hexaethyl tetraphosphate, 1 pint of a 50-percent formulation in 100 gallons of water, killed 90 percent in 42 hours, whereas 40-percent nicotine sulfate solution, 1.6 pints in 100 gallons of water, killed only 25 percent. Fewer aphids were collected on potato foliage following the application of hexaethyl tetraphosphate than when nicotine sulfate was used.--Chapman, Voss and Allen (**). 2/

In greenhouse tests 0.3 gram of hexaethyl tetraphosphate per 1,000 cubic feet distributed as an aerosol from a 10-percent solution in methyl chloride killed 100 percent of the aphids.--Smith et al. (14).

Myzus circumflexus (Buck.), the crescent-marked lily aphid

Myzus convolvuli (Kltb.), the foxglove aphid

Myzus dianthi (Schrank)

Same as for Macrosiphum solanifolii (Ashm.).--Smith et al. (14).

Myzus persicae (Sulz.), the green peach aphid

In greenhouse tests 0.3 gram of hexaethyl tetraphosphate per 1,000 cubic feet distributed as an aerosol from a 10-percent solution in methyl chloride killed 96 percent of the aphids; twice this concentration killed 96 percent, and 1 to 2.5 grams killed 100 percent.--Smith et al. (14).

Rhopalosiphum rufomaculatum (Wilson), the green chrysanthemum aphid

Same as for Aphis gossypii Glov.--Smith et al. (14).

2/ Two asterisks (**) indicates an unpublished report submitted to the Wisconsin Agricultural Experiment Station, December 31, 1946.

Unidentified aphids

Bladan at a concentration of 0.06 percent of hexaethyl tetraphosphate is very effective against aphids.--Hall (6); Kilgore (8).

Hexaethyl tetraphosphate has given promising results against aphids on citrus in California.--Boyce (*).

Cicadellidae

Empoasca fabae (Harr.), the potato leafhopper

Hexaethyl tetraphosphate in sprays (1:1600) and dusts (5-percent) showed considerable toxicity to the potato leafhopper in field plot tests in Wisconsin.--Chapman, Voss and Allen (**).

Macrostelus divisus (Uhl.), the six-spotted leafhopper

A spray of hexaethyl tetraphosphate 1:800 showed considerable toxicity, being more effective than DDT, 2 pounds in 100 gallons of water, based on counts of leafhoppers at the end of 1 day.--Chapman, Voss and Allen (**).

Coccidae

Coccus pseudomagnoliarum (Kuw.), the citricola scale

A proprietary preparation containing 50 percent of hexaethyl tetraphosphate used at the rate of 1 pint in 100 gallons of water applied during late summer with thorough coverage gave a high degree of kill of immature citricola scale on oranges in California.--Boyce (*).

Phenacoccus gossypii T. and C., the Mexican mealybug

Pseudococcus citri (Risso), the citrus mealybug

In greenhouse tests 1 to 2.5 grams of hexaethyl tetraphosphate per 1,000 cubic feet, distributed as an aerosol from a 10-percent solution in methyl chloride, killed 97 percent of the Mexican mealybugs and 64 percent of the citrus mealybugs.--Smith et al. (14).

Psyllidae

Psylla pyricola Foerst, the pear psylla

Hexaethyl tetraphosphate, 8 ounces to 100 gallons of spray with 2 ounces of B-1956 (a phthalic glyceryl alkyd resin) effectively controlled nymphs on pears in the Hudson River Valley. A 50-percent commercial material used at 16 ounces to 100 gallons also effectively controlled nymphs. When 1 gallon of summer oil was added to this spray mixture, large numbers of adults were killed.--Hamilton (*).

In small-scale field tests at Spokane, Wash., hexaethyl tetraphosphate compared favorably with nicotine for the control of the pear psylla.--Bishopp (3).

HEMIPTERA

Miridae

Lygus sp., plant bugs

A 3-percent hexaethyl tetraphosphate dust applied at the rate of 40 pounds per acre for the control of Aphis rumicis on stringless pole beans also killed plant bugs.--Hanna (*).

COLEOPTERA

Chrysomelidae

Diabrotica duodecimpunctata (F.), the spotted cucumber beetle

Applied as dusts in Wisconsin tests, hexaethyl tetraphosphate did not compare favorably with DDT.--Chapman, Voss, and Allen (**).

Epitrix cucumeris (Harr.), the potato flea beetle

In field plot tests in Wisconsin hexaethyl tetraphosphate 1:1600 was inferior to DDT or benzene hexachloride at 0.5 pound per 100 gallons of water. It was also inferior to DDT when both were tested as 5-percent dusts.--Chapman, Voss, and Allen (**).

Coccinellidae

Ladybeetles

A 3-percent hexaethyl tetraphosphate dust, applied at the rate of 40 pounds per acre for the control of Aphis rumicis on stringless pole beans, killed ladybeetles.--Hanna (*).

LEPIDOPTERA

Phalaenidae

Trichoplusia ni (Hbn.), the cabbage looper

See Pieris rapae.

Pieridae

Pieris rapae (L.), the imported cabbage worm

Applied as a 5-percent dust and as an aqueous spray, 1:800, hexaethyl tetraphosphate showed no toxicity to these imported cabbage insects in tests in Wisconsin.--Chapman, Voss, and Allen (**).

Plutellidae

Plutella maculipennis (Curt.), the diamondback moth

An application of a 3-percent hexaethyl tetraphosphate dust at the rate of 45 pounds per acre to a field of cauliflower caused a mortality of 54 percent of cabbage worms and diamondback moth larvae.-- Hanna (*).

Olethreutidae

Carpocapsa pomonella (L.), the codling moth

In laboratory tests using the apple-plug method an aqueous solution of hexaethyl tetraphosphate (1 pound per 100 gallons) caused 100-percent mortality of the larvae and half this concentration caused 93- to 98-percent mortality.--Siegler and Hall (12).

DIPTERA

Drosophilidae

Drosophila sp.

In laboratory tests conducted by Metcalf in California, hexaethyl tetraphosphate had a median lethal concentration of 0.00075 percent.--Bishopp (3).

ACARINA

Tarsonemidae

Hemitarsonemus latus (Banks), the broad mite

In greenhouse tests 1 to 2.5 grams of hexaethyl tetraphosphate per 1,000 cubic feet, distributed as an aerosol from a 10-percent solution in methyl chloride, killed no mites.--Smith et al. (14).

Tetranychidae

Paratetranychus citri (McG.), the citrus red mite

Hexaethyl tetraphosphate applied as sprays, dusts, and thermal aerosols has given promising results in killing the active forms of the citrus red mite on citrus in California. However, no effect on the egg and no appreciable residual effect were observed.--Boyce (*).

In laboratory tests by Metcalf in California, hexaethyl tetraphosphate had a median lethal concentration of 0.0075 percent.--Bishopp (3).

Tetranychus bimaculatus (Harvey), the two-spotted spider mite

In laboratory tests an aqueous solution of 0.025 percent of hexaethyl tetraphosphate and 0.05 percent of sodium lauryl sulfate killed 97 percent of the nymphs and adults.--Siegler and Hall (12).

In greenhouse tests 0.3 gram of hexaethyl tetraphosphate per 1,000 cubic feet distributed as an aerosol from a 10-percent solution in methyl chloride killed 67 percent of the mites; twice this concentration killed 72 percent and 1 to 2.5 grams killed 98 percent.--Smith et al. (14).

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